



Short communication

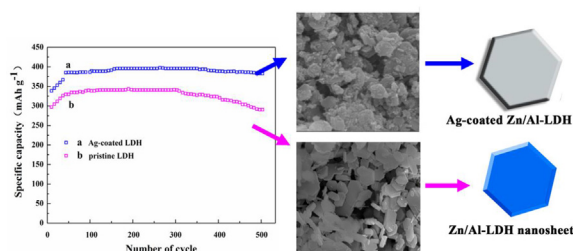
Facile synthesis of novel two-dimensional silver-coated layered double hydroxide nanosheets as advanced anode material for Ni–Zn secondary batteries

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HIGHLIGHTS

- Ag-coated nanosheets have been successfully prepared by a silver mirror reaction.
- The 2D Ag-coated nanosheet was used for Ni–Zn secondary cell applications.
- The anode with Ag-coated LDH reveals a significantly improved cyclability.
- Capacity retention of battery after 500 cycles is improved from 83% to 98%.
- The improvement is attributed to the excellent electron conductivity of Ag-coating.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver-coated layered double hydroxide (Ag-coated LDH) nanosheets are successfully prepared by a facile silver mirror reaction and their electrochemical performance has been evaluated as anode materials for Ni–Zn secondary batteries. The microstructure and morphology of as-prepared Ag-coated Zn/Al-LDH are investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). As anode material for Ni–Zn secondary batteries, Ag-coated Zn/Al-LDH exhibits high specific capacity (400 mAh g⁻¹), good charge–discharge properties and excellent cycling performance, which is attributed to the effect of the electron conductivity improvement by the Ag coating on the surface of Zn/Al-LDH nanosheet. This newly designed Ag-coated Zn/Al-LDH may offer a promising anode candidate for high-performance Ni–Zn secondary batteries.

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1. Introduction

Zn–Ni alkaline secondary system is a promising candidate for the new generation of green power sources used in electric vehicle

(EV) or hybrid electric vehicle (HEV) in recent years, due to its high specific energy, excellent specific power and high open-circuit voltage. It is low cost, non-toxic, more environmentally friendly than many other battery systems, and it can be used within a wide temperature range [1–6]. Recently, development of Ni–Zn rechargeable battery system has made this technology viable and competitive with other commercially available rechargeable battery systems [1,5–7]. However, the most critical problems of Ni–Zn

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rechargeable batteries are shape change and dendrite formation on the negative side resulting in poor cycling efficiency and electrical short, which limit their widespread commercialization [1,4,7]. Shape change and dendrite formation refer to the reduction of the electrochemically active surface area of the ZnO electrode during repeated cycling of the battery, as a result of the redistribution of ZnO material over the electrode. To solve the shape change and dendrite formation, the essential method is to inhibit the dissolution of ZnO into the alkaline electrolyte. Up to now, great many attempts have been undertaken by using various additives like TiO_2 [1], Ca(OH)_2 [3,8], SnO_2 [4], and In_2O_3 [9] physical mixed with the ZnO electrode. The essential approach is to inhibit the dissolution of ZnO into the alkaline electrolyte, but the physical mixture could not suppress the dissolution enough and the utilization of additive is relatively low. The secondary zinc electrodes based on the calcium zincate as active material have also been studied. For examples, Yang et al. [3] have studied the electrochemical properties of calcium zincate by mechanical ball milling of ZnO and Ca(OH)_2 on a secondary Ni–Zn cell. Zhang et al. [8] have investigated the chemically co-precipitated calcium zincate as anode active material. However, the discharge capacity of calcium zincate electrode is relatively too low, which is only about 280 mAh g^{-1} , due to the content of Ca(OH)_2 in zinc electrode is relatively high, which results in a decline in the electrode capacity [4].

Recently, substantial efforts have been devoted to the replacement of the conventional anode active material ZnO for Ni–Zn secondary batteries with alternatives that allow good cycling stability and improved electrochemical performance [1,5,10]. Layered double hydroxides (LDH), a family of layered inorganic compounds consisting of stacks of positively charged metal hydroxide layers with anions in the interlayer (Zn/Al-LDH structure shown in Fig. 1), have been widely studied in fields of catalysts, drug delivery materials, nanofillers, electrode materials and chemically tailored functional materials [5,11–13]. In particular, LDH is capable of undergoing an inner redox reaction within a limited potential range in alkaline medium. In our recent studies, we investigated the application of Zn/Al layered double hydroxide (Zn/Al-LDH) as a novel anode material for Ni–Zn secondary cells for the first time [7]. Although the Zn/Al-LDH anodes showed better cycling

performance than pure ZnO anodes, these anodes have the drawback of the low conductivity of Zn/Al-LDH, which is unfavorable to electron transfer and consequently impacts the electrochemical performance of the anode. To overcome this problem, it is very desirable to develop an electrochemical active and good conductivity material for Ni–Zn secondary cells. During the last few years, there were some researches dealing with the silver depositing on the battery active materials such as LiFePO_4 [14], $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [15], LiMn_2O_4 [16], silicon [17] and carbon [18], and improved electrochemical performance was achieved, which was mainly ascribed to fact that the deposited Ag nanoparticles on their surface efficiently increased the electrical conductivity of the material particles and reduced the charge-transfer resistance during the charging and discharging processes.

In this report, Zn/Al-LDH nanosheets prepared by a co-precipitation process were coated with silver nanoparticles by the traditional silver mirror reaction. The as-prepared Ag-coated Zn/Al-LDH samples were used as anode materials for Ni–Zn battery, whose charge–discharge properties, electrochemical impedance spectroscopy and cycle performances were examined in detail. Interestingly, the charge–discharge tests demonstrated that the electrodes with Ag-coated Zn/Al-LDH nanosheets exhibited a relatively high capacity and excellent cycleability when they were used as anodes of Ni–Zn battery. To the best of our knowledge, this is the first report regarding the conductive 2D Ag-coated LDH nanosheets for anode active material in battery.

2. Experimental

2.1. Preparation of pristine LDH and Ag-coated LDH

All the chemicals were of analytical grade and were used without further purification. Pristine LDH (Zn/Al-LDH) was prepared by a co-precipitation method. In a typical procedure, an alkaline solution (100 ml) containing NaOH (0.5 M) and Na_2CO_3 (0.1 M) was titrated with 100 ml of a salt solution of $\text{Zn(NO}_3)_2$ (0.2 M) and $\text{Al(NO}_3)_3$ (0.05 M) with $\text{Zn}^{2+}/\text{Al}^{3+}$ molar ratio of 4:1 under vigorous stirring at 65°C . The pH value of the solution was adjusted to 10 by further titration with 1 M NaOH solution. Thereafter, the slurry was transferred into a 100 ml Teflon-lined autoclave at 120°C for 20 h. Finally, the obtained product was filtered and washed with deionized water and ethanol several times followed by vacuum-drying at 60°C for 10 h.

The Ag-coated Zn/Al-LDH was fabricated by the traditional silver mirror reaction, as illustrated in Fig. 2. First, AgNO_3 aqueous solution (10 ml, 0.01 M) was dissolved in 50 ml distilled water in a beaker. Then aqueous ammonia was added dropwise to an AgNO_3 solution, until a clear colorless solution was obtained. Subsequently, the obtained LDH (Zn/Al-LDH) (0.2 g) was added into the obtained ammonia/ AgNO_3 solution with agitated stirring. The glucose aqueous solution (10 ml, 0.4 M) was then added dropwise

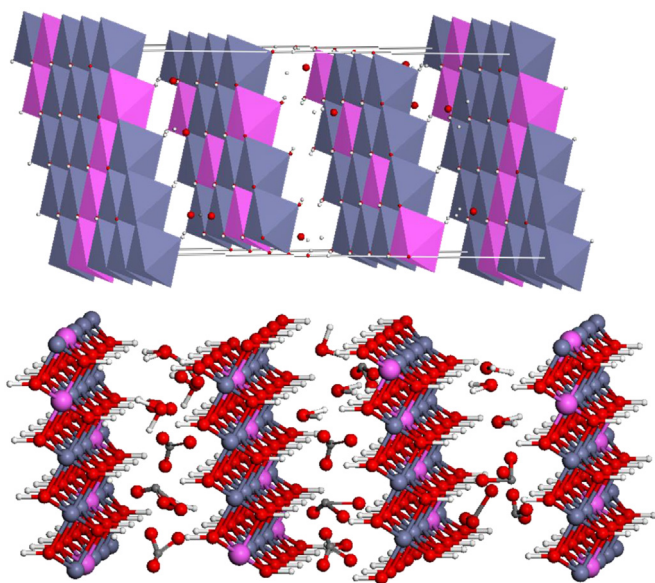


Fig. 1. The structure of Zn/Al-LDH, $\text{Zn}_4\text{Al}_2(\text{OH})_{20}[\text{CO}_3^{2-}]$, is a clay with cationic layers and charge-balancing anions.

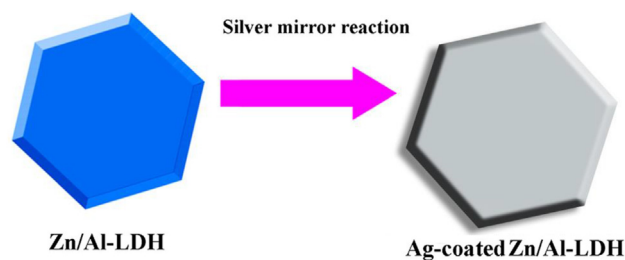


Fig. 2. A schematic illustration of the formation process of Ag coating on the surface of Zn/Al-LDH.

to the solution, followed by agitated stirring for 1 h. Finally, the sample was washed with distilled water and desiccated in a vacuum oven at 60 °C for 12 h.

2.2. Structural characterization

The structure of the obtained Zn/Al-LDH and Ag-coated Zn/Al-LDH was characterized by X-ray diffraction (XRD) (Philips) using Cu K α radiation at 35 kV and 200 mA, $\lambda = 1.5406$ Å. SEM investigations were performed using a JEOL 6300F field-emission scanning electron microscope (JEOL, Tokyo, Japan). HRTEM (JEOL 4000EX, JEOL, Tokyo, Japan) was used to study the morphology and microstructure of the samples. EDX analyses were performed using an EDAX system (EDAX, Mahwah, NJ, USA).

2.3. Electrochemical measurements

The anodes (zinc electrode) were prepared by pasting a mixture consisting of 80 wt.% as-prepared active material, 10 wt.% conductive acetylene carbon black, and 10 wt.% polytetrafluoroethylene (PTFE, 5 wt.%, in diluted emulsion) binder on a copper mesh substrate (1 × 1 cm in size) served as the current collector. The loading of every electrode is about 0.1 g. The obtained anodes were dried under vacuum at 60 °C for 12 h and then roll-pressed to a thickness of ~0.3 mm to enhance the contact between the active materials and the conductive copper mesh substrate.

The cathode was the commercial sintered Ni(OH) $_2$ (Tianjin City Fine Chemical Research Institute) electrode whose capacity was far higher than those of the zinc electrodes, so the capacity obtained in this present work just reflected the performance of anode (Ag-coated Zn/Al-LDH or bare Zn/Al-LDH). An aqueous solution of 6 M KOH saturated with ZnO was used as the electrolyte. Solid electrodes separated by the liquid electrolyte were kept apart by an electrolyte-permeable separator. Multilayer polypropylene micro-porous membranes (Celgard®) were used as the separator to prevent the electrodes from shorting. Because this separator is hydrophobic, it can be use in aqueous alkaline conditions after specially treated by soaking in the lubricant (iso-paraffin solvent) for 24 h. The zinc anode, Ni(OH) $_2$ cathode, separator and electrolyte were placed in a simple battery container made by ourselves and assembled into a battery, as shown in Fig. 3.

The galvanostatic charge–discharge tests were conducted on a Neware battery test system (NEWARE BTS-610, Neware Technology Co. Ltd., China) at room temperature. The cells were charged at 1C for 1 h, and then discharged at 1C down to a cut-off voltage of 1.2 V. Electrochemical impedance spectroscopy (EIS) measurements were

performed on a CHI 640B type electrochemical system (Shanghai). The frequency range applied was between 0.01 Hz and 100 KHz with amplitude of 10 mV. A three electrode cell assembly was used with a Hg/HgO electrode as reference, a Ni(OH) $_2$ electrode as counter-electrode and an electrode with Zn/Al-LDH or Ag-coated Zn/Al-LDH of as working electrode. The electrolyte was ZnO-saturated 6 M KOH solution.

3. Results and discussion

3.1. Characterization of the Ag-coated LDH nanosheets

Fig. 4 shows the powder XRD patterns of as-prepared Zn/Al-LDH and Ag-coated Zn/Al-LDH samples. The XRD patterns of both samples display the characteristic reflections corresponding to two-dimensional hydrotalcite-like materials, such as (003), (006), (012), (015), (018) and (110) in each case, indicative of $R\bar{3}m$ symmetry and a hexagonal lattice. The sharp basal reflection series of both the pristine Zn/Al-LDH and Ag-coated Zn/Al-LDH indicate a well-crystallized structure for the two nanoparticles. The peaks located at 37.85°, 45.15°, and 64.26° can be assigned to (111), (200), (220) crystal faces of Ag (JCPDS, File No. 04-0783).

The morphology and microstructure of the as-prepared Zn/Al-LDH and Ag-coated Zn/Al-LDH samples were characterized by SEM and TEM. In Fig. 5a, the Zn/Al-LDH sample typically consists of uniform and thin hexagonal platelets with a very smooth surface. As seen in Fig. 5b and d, the surface of the Ag-coated Zn/Al-LDH nanosheets is not as smooth as pristine Zn/Al-LDH nanosheets and shows a more uneven surface, which provides the supporting evidence as Ag nanoparticles are deposited uniformly on the surface of Zn/Al-LDH nanosheets and form a uniform Ag coating by this traditional silver mirror reaction. This microstructure facilitates the electronic transfer among the Zn/Al-LDH nanosheets. The existence of Ag coating on the surface of Ag-coated Zn/Al-LDH nanosheet is also identified by EDS and HRTEM, as shown in Fig. 5c and f. The Ag-coated Zn/Al-LDH synthesized in this work contains 5.69 wt.% Ag determined by the EDS analysis.

3.2. Electrochemical measurements

Fig. 6a presents the cycle performance curves of the un-coated Zn/Al-LDH and the Ag-coated Zn/Al-LDH cycled at a current

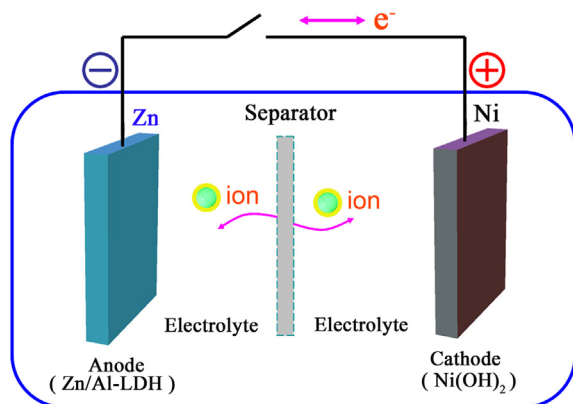


Fig. 3. Schematic illustration of our Ni–Zn battery.

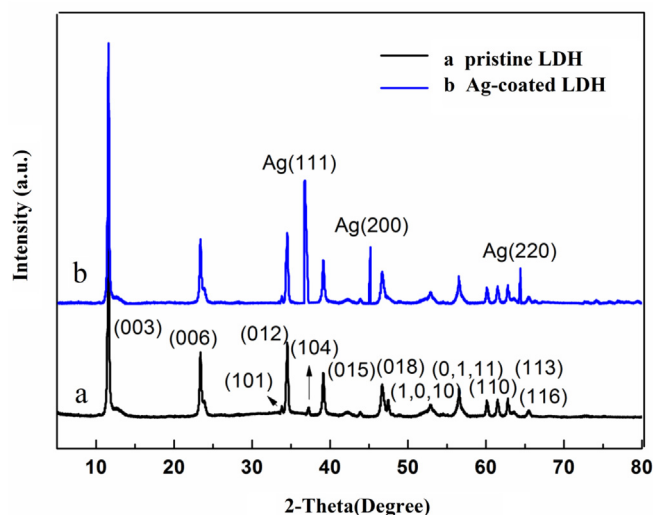


Fig. 4. The XRD patterns of Zn/Al-LDH and Ag-coated Zn/Al-LDH.

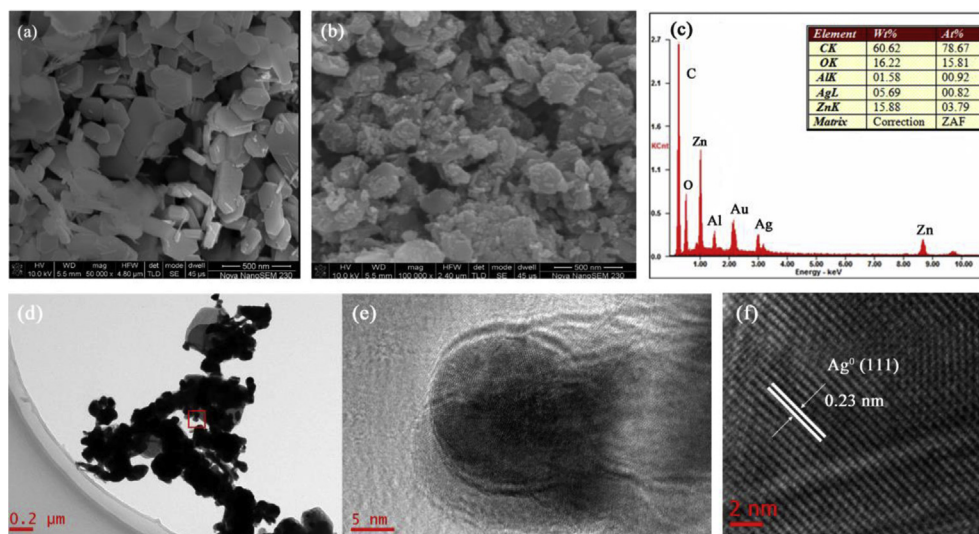


Fig. 5. SEM images of (a) Zn/Al-LDH and (b) Ag-coated Zn/Al-LDH; (c) EDS spectrum of Ag-coated Zn/Al-LDH; (d) TEM image of Ag-coated Zn/Al-LDH; (e, f) HRTEM images of a single Ag nanoparticles marked in Fig. 5d.

density of 420 mA g^{-1} over the voltage range of 1.2–1.9 V. The capacity retention for the Ag-coated Zn/Al-LDH is measured to be as high as 98% of the highest discharge capacity after the 500th cycle, which, in contrast, is only 83% for the Ag-free Zn/Al-LDH electrode. And the discharge capacity of the Ag-coated Zn/Al-LDH (5.69 wt.% Ag) is always about 400 mAh g^{-1} higher than that of uncoated Zn/Al-LDH, and much stable even throughout 500 cycles. And the weight of each zinc electrode was examined after the cycling test. The weight loss of the un-coated Zn/Al-LDH electrode

is 20%. However, the Ag-coated Zn/Al-LDH electrodes did not observe the obvious weight loss. The cycle stability is the most important performance for Ni–Zn batteries. The above results obviously indicate that Ag-coated Zn/Al-LDH has a better cycle stability than pristine Zn/Al-LDH and it is evident that Ag coating can significantly improve the cycle performance of anode. For the Ag-coated Zn/Al-LDH, the loaded silver nanoparticles are uniformly distributed on the Zn/Al-LDH surface and incorporated evenly an Ag coating, which could effectively decrease the charge-transfer

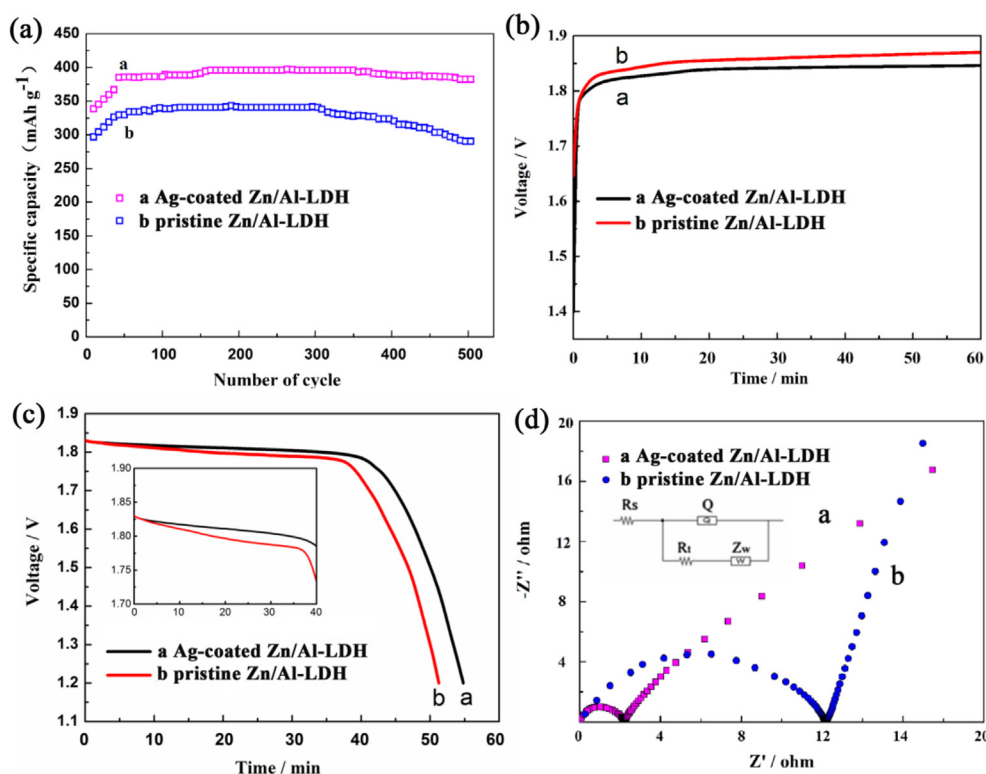


Fig. 6. (a) Cycling performance of the Zn/Al-LDH and Ag-coated Zn/Al-LDH; (b, c) typical charge/discharge curves of Zn/Al-LDH and Ag-coated Zn/Al-LDH as anode active materials at the 100th cycle; (d) EIS analysis of Zn/Al-LDH and Ag-coated Zn/Al-LDH electrodes.

resistance of anode for Zn–Ni batteries, and marvelously improve the discharge capacity and cycling stability of Zn/Al-LDH nanosheets.

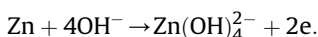
The typical charge–discharge curves of Zn–Ni cells with Ag-coated and un-coated Zn/Al-LDH tested at the 100th cycle are displayed in Fig. 6b and c. We can find that the charge–discharge coulombic efficiencies are less than 100% for both cells. To the secondary alkaline zinc batteries, the charge capacity of zinc negative electrode is decided by the theoretical capacity of zinc electrode (in the present work, the theory capacity of Zn/Al-LDH is 420 mAh g^{−1}). So the charge capacity of zinc electrode is just the theoretical capacity, but the discharge capacity of zinc electrode is the practical capacity when battery discharged. Therefore, the coulombic efficiencies of zinc negative electrodes (coulombic efficiency = discharge capacity/charge capacity) are less than 100%, because the practical discharge capacity can't absolutely reach to the theoretical capacity. In the present work, the coulombic efficiencies of Zn/Al-LDH and Ag-coated Zn/Al-LDH are 83% and 91.5%, respectively. In addition, the practical discharge capacity is affected by the electric conductivity and particle morphologies of active material. So the coulombic efficiency of Ag-coated Zn/Al-LDH is higher than Zn/Al-LDH.

In our simulated battery, the capacity of Ni(OH)₂ cathode is far higher than that of the zinc anode (it would make sure that the capacities of cells was controlled by zinc anode), and the change trend of the potential of Ni(OH)₂ cathodes is always the same under the same test condition (that means the potential of Ni(OH)₂ cathode is a certain constant value at a fixed time when charge or discharge). In our different test cells, the cathode is always the same, and the only difference is the zinc anode (with or without Ag coating). According to the equation:

$$V_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}},$$

the E_{cathode} is a constant value at a fixed time, so the work voltage of a full cell (V_{cell}) can reflect the performance of the zinc anode potential (E_{anode}). So the role of Ni(OH)₂ cathode is a little like a reference electrode and keeps a constant value at a fixed time in our simulated battery. Therefore, it's clear that the cell voltage (V_{cell}) in Fig. 6b and c can reflect the performance of negative electrode potential (E_{anode}).

For the Ag-coated Zn/Al-LDH, the cells show lower charge plateau voltage and high discharge plateau voltage. And the potential fading of un-coated Zn/Al-LDH is faster than that of Ag-coated Zn/Al-LDH. The decrease in charge plateau voltage conduces to the suppression of H₂ formation, the improvement of charge efficiency and an enhancement of active material utilization in the anodes [1]. From Fig. 6b, it is clearly found that the Ag-coated Zn/Al-LDH is more effective than pristine Zn/Al-LDH. The discharge voltage is an important parameter for batteries. Higher discharge voltage associates with higher specific power and better cell performance [2]. From Fig. 6c, the difference in the discharge voltage is not notable in 0–20 min range, but the difference in the discharge voltage becomes obvious and large after 20 min. The reason is as follow: in the discharge process, the zinc electrode reaction can be described as:



At the beginning of discharge progress, the difference in the discharge voltage between the pristine Zn/Al-LDH and Ag-coated Zn/Al-LDH is not noticeable, because the conductivity of the both zinc electrodes is good by the absence of a mount of Zn metal in the zinc electrodes. But with the discharge time increasing, the Zn

metal in the electrode is gradually changed to Zn²⁺, and the conductivity of pristine Zn/Al-LDH electrode becomes much lower. For the Ag-coated Zn/Al-LDH, although the Zn metal in the electrode is gradually changed to Zn²⁺, the conductivity of zinc electrode with Ag-coated Zn/Al-LDH is still good by the high electrical conductivity of the Ag coating. Therefore, the discharge voltage of Ag-coated Zn/Al-LDH is significantly higher than that of un-coated Zn/Al-LDH after 20 min. And the enhanced discharge capacity and time could be attributed to an enhanced electrical conductivity and a decreased inner resistance of the anodes. In addition, the formation of a thin Ag coating layer on the surface of the Zn/Al-LDH particles can also prohibit the direct contact of the active core material with the alkaline electrolyte and minimize the side reactions within the batteries. The increase in discharge voltage should be attributed to the decreases of the anode resistance R_{anode} , which comes from the good conductivity of the Ag-coating on the surface of LDH nanosheet, according to the equation [2]:

$$V = E_{\text{cathode}} - E_{\text{anode}} - I(R_{\text{Qanode}} + R_{\text{Qcathode}} + R_{\text{Qelectrolyte}} + R_{\text{Qother}}) \quad \text{discharging mode} \quad (1)$$

$$V = E_{\text{cathode}} - E_{\text{anode}} - I(R_{\text{Qanode}} + R_{\text{Qcathode}} + R_{\text{Qelectrolyte}} + R_{\text{Qother}}) \quad \text{charging mode} \quad (2)$$

Fig. 6d shows the analysis of electrochemical impedance spectroscopy (EIS), which can provide important information about the electrochemical system, such as the evaluation of charge transfer parameters and bulk electrolyte properties. Typically, the plot consists of semicircles which can be attributed to charge transfer processes, and a sloped line that is related to the mass transfer of ions. The Ag-coated Zn/Al-LDH electrode has a charge-transfer resistance (R_{CT}) of 2.12 Ω, much smaller than that of the un-coated Zn/Al-LDH electrode (12.20 Ω). Such a small charge-transfer resistance was ascribed to the Ag coating, which provides high electronic conductivity for the Zn/Al-LDH material and thus results in faster electron transportation.

4. Conclusion

Surface decoration of Zn/Al-LDH nanosheets with Ag coating was performed by the traditional silver mirror reaction. The as-prepared Ag-coated Zn/Al-LDH demonstrates high discharge capacity, good charge–discharge performance and excellent cycle stability. This superior electrochemical performance is attributed to the anchored Ag coating that increases the electronic conductivity of anode. The EIS of Ag-coated Zn/Al-LDH shows the much small high-frequency capacitive semicircular loop radius, which indicates that the Ag coating can remarkably decrease the charge-transfer resistance and improve the activity of anode material. These results indicate that Ag-coated Zn/Al-LDH nanosheets are well suited for the anode active material for Ni–Zn batteries.

Acknowledgments

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